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OLIVE MILL WASTEWATER TREATMENT BY A PILOT-SCALE SUBSURFACE HORIZONTAL FLOW (SSF-h) CONSTRUCTED WETLAND

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Summary - Performances of a pilot-scale reed bed for the olive mill wastewater (OMW) treatment were investigated, by monitoring influent and effluent pH, total suspended solids (TSS), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total phosphorus and polyphenols. In order to reduce the suspended matter concentration and to avoid clogging, OMW was pre-treated by adding lime putty, calcium hydroxide and hydraulic lime. The best results were obtained with 2 g/L of hydraulic lime. Pre-treated OMW was dosed in the reed bed at dilution ratios of 1/3 and 1/10 (v/v), pointing up that the latter only did not give rise to reed suffering and allowed to obtain good and durable removal efficiencies, above all for COD ($74.1 \pm 17.6\%$) and polyphenols ($83.4 \pm 17.8\%$). Recycling of the effluent was quite effective for the improvement of the wastewater quality, allowing a further removal of 26-70%, depending on the parameter taken into account. A post-dosage study, carried out by feeding the reed bed with the effluent of an activated sludge plant, pointed up a rapid decreasing of the outlet concentrations of the investigated parameters to values compatible with Italian regulations concerning wastewater discharge in surface water. Polyphenols were the exception, being their outlet concentration at the end of post-dosage study around 2 mg/L.

INTRODUCTION

Olive mill wastewater (OMW) is an industrial sewage produced during the olive-oil extraction. Olive oil is extracted from olive pulp (obtained by grinding the drupes in stone mills), mainly by two different systems, pressing or three-phase centrifugation. According to the first method, the pulp is pressed in a filter-press obtaining a mixture of oil and OMW, which are separated by decantation. In the centrifugation method the pulp is continuously pumped in a three phase decanter, where oil, OMW and the solid olive residue are separated.

OMW shows different characteristics depending on several parameters such as the variety of olives, their ripening level, the climatic and soil conditions and the extraction method;¹ it is an aqueous, dark, foul-smelling and turbid suspension having a very high organic load (COD = 15-390 g/L), an

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acid pH (4.6-5.8) and a significant content of phytotoxic and antibacterial phenolic substances (total polyphenols = 1.5-14 g/L).^{2,3}

Such a composition makes the treatment and/or the disposal of OMW a critical environmental problem, especially in the Mediterranean area, where olive agriculture is widespread and a large volume of OMW is produced over a relatively short period of time (usually from November to February). During this period, in fact, about 11 million tons of olives are processed, giving rise to about 9 million tons of OMW.⁴

Several methods have been tested for OMW treatment such as incineration, electrochemical oxidation, stabilization ponds, thermal concentration and other physico-chemical and aerobic and anaerobic biological treatments, as well as direct discharge to the soil.⁵⁻¹⁰ However, most methods are very expensive and give rise to sludge or other by-products, which need to be further disposed or treated.¹¹

For these reasons, the management of OMW by land application, which has been regulated in Italy from 1996 (L. 574/96), still represents the simplest and cheapest OMW disposal method, although phytotoxic effects on soil have been observed.¹²⁻¹⁴

Horizontal subsurface (SSF-h) constructed wetlands have been extensively used for the treatment of domestic wastewater¹⁵⁻¹⁷ and, less frequently, of industrial sewage^{18,19}. The use of SSF-h systems for OMW disposal can be assimilated to a direct discharge to the soil, carried out in completely controlled conditions of sewage application and without any pollution risk for agricultural soils and groundwater.

Despite the potential benefits which could be expected from the use of SSF-h reed beds for OMW treatment, there is a lack of data about their ability in OMW pollutant removal. Therefore, this paper aims to study the treatment of OMW in a pilot scale SSF-h constructed wetland planted with *Phragmites australis*, by testing different pre-treatment methods and dilution ratios, in addition to the effect of effluent wastewater recycling.

The following chemical parameters have been monitored: pH, total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD₅), polyphenols, total phosphorus and total Kjeldahl nitrogen (TKN, the sum of organic and ammonium nitrogen).

EXPERIMENTAL

The wastewater used in this investigation was obtained from an olive oil extraction plant operating with a pressing method and located in Impruneta (Florence, Italy).

Materials for OMW pre-treatment

OMW samples were pre-treated in order to reduce the concentration of suspended solids and, therefore, to avoid clogging. Calcium hydroxide (Merck), lime putty and hydraulic lime (Fornace di calce Fagotti, Mercatale V.P., Florence, Italy) were added at different concentrations to the OMW. The obtained mixtures were stirred for 30 minutes and finally settled in Imhoff cones for 24 hours. Afterwards, an aliquot of the upper phase was collected and analysed for pH, COD, BOD₅ and TSS.

Site Description.

The investigation was carried out from March to November 2001, in a pilot-scale SSF-h system situated at Florence, operating since 1997 as a secondary treatment of domestic wastewater.¹⁵

The plant was a Plexiglas basin (12 mm thick), placed above ground-level and protected by movable polyurethane panels (40 mm thick) around the outside, in order to avoid algae growth on the interior walls of the cell.

The pilot plant (basin slope 1%) was covered with a nylon-tarpaulin to avoid dilution effects due to rain water, but still maintaining the solar exposure.

The area and depth of the SSF-h system were 0.85 m^2 and 0.6 m , respectively. Grain sizes and composition of the filling media were the same elsewhere reported.¹⁵

Hydraulics of the system

The operational scheme of the system is shown in Figure 1.

Experimental hydraulic retention time (HRT), calculated at the start of the study, was 3 days, although it increased in the summer period as a consequence of evapotranspiration phenomena.

The inlet flow was adjusted and daily controlled to $0.024 \text{ m}^3/\text{d}$ by a peristaltic pump sucking from a 250 L-polyethylene dosing tank continuously stirred (see Figure 1).

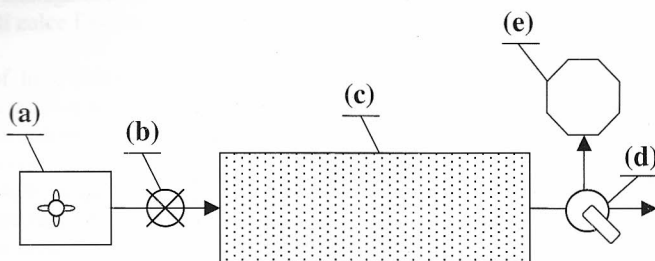


FIG. 1 - Operational scheme of the pilot system. (a) OMW tank and mechanical stirrer; (b) peristaltic pump; (c) reed bed; (d) three way valve; (e) outlet collection tank.

The outlet flow was monitored during five measurement campaigns pointing out its strong variation according to the change of wetland temperature. In particular, a significant decrease was observed in July, September and, above all, in August, when strong evapotranspiration phenomena took place. Since a decrease in outlet flow causes an artificial increase of the concentration of the measured parameters, average flow data were plotted as a function of the mean wetland temperatures and fitted by an exponential function (see Figure 2), in order to transform concentration units in mass units.

Sampling and analyses

The HRT was calculated at the start of the study by monitoring the effluent absorbance at $\lambda=281 \text{ nm}$, which represent a specific absorption wavelength of ultraviolet-visible spectra of polyphenols.³ Wetland temperature was measured continuously *in situ* by a thermocouple (WTW Instruments) and registered every hour; daily values are the mean of 24 measures.

Inlet and outlet wastewaters were sampled (usually twice every week) and, within a hour from the collection, filtered on glass fibre filter (GF/F, Whatman, porosity $\approx 0.45 \mu\text{m}$, England). Total suspended solids (TSS) were determined gravimetrically.²⁰

Analysis of total Kjeldahl nitrogen (TKN) was carried out spectrophotometrically, after digestion of the sample, by the Hach Nessler method.²¹

Total phosphorus was analysed according to the Hach acid persulfate digestion method.²²

Chemical oxygen demand was determined both on filtered (COD_S) and unfiltered (COD_T) samples according to the IRSA-CNR method.²³

Biological Oxygen Demand was quantified on unfiltered samples by using the OxiTop® system (WTW Instruments), after inhibition of the nitrification reaction by adding N-allylthiourea and incubation for five days in darkness at 20°C (BOD_5).

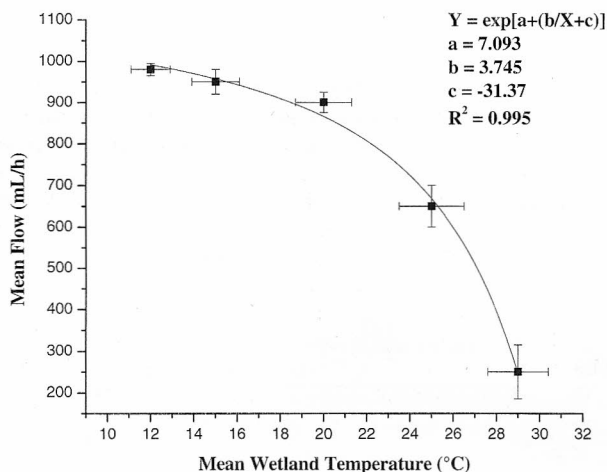


FIG. 2 - Exponential regression analyses describing the relationship between mean outlet flow data and mean wetland temperatures. Error bars represent the standard deviation of the average experimental flow and wetland temperature.

Analysis of total polyphenols was carried out according to the following procedure, adapted from Visioli et al.²⁴: 10 ml-aliqouts of OMW were acidified with 1M HCl up to about pH=2 and extracted three times, each with 5 ml of ethyl acetate. Under these experimental conditions a recovery of about 90% from standard solutions of caffeic acid was obtained. In addition, recovery tests carried out on OMW showed that a further extraction accounted for only 4% of the first three extractions.

The extracts were combined, dried over anhydrous sodium sulphate and a 0.8 ml-aliqout was evaporated to dryness under a gentle nitrogen stream. Then, 0.8 ml of methanol, 0.2 ml of Folin-Ciocalteu reagent (Merck) and 0.4 ml of a saturated solution of Na₂CO₃ were added. The obtained solution was made up to 10 ml with ultra pure water (MilliQ System, Millipore Instruments) and spectrophotometrically analysed at 725 nm, in parallel with a blank, after 1 hour of darkness incubation and centrifugation at 1500 rpm for 15 minutes. The concentration of total polyphenols was calculated on the basis of a calibration line obtained from standard solutions of caffeic acid and corrected according to the recovery percentage.

Spectrophotometric measurements were performed by a DR2010 spectrophotometer (Hach Instruments).

Analysis of pH was carried out by a pH-meter pH340i (WTW Instruments).

Recycling of effluent wastewater

Effluent wastewater from the experiment at a dilution ratio 1/10 v/v was stored in a dark room until its use in the recycling test.

RESULTS AND DISCUSSION

OMW pre-treatment

The chemical characteristics of the OMW used in this study were reported in Table 1. It showed an acid pH and a high content of solids and of organic carbon. BOD₅ represented only about 20% of the COD_T, meaning that only a small fraction of the organic carbon is readily degradable in OMW *per se*. This is in agreement with the well-known antimicrobial characteristics of OMW, that make this sewage very poor of biomass.^{25,26}

In order to reduce the concentration of suspended solids, which can cause critical problems in the hydraulic management of the plant, calcium hydroxide (Merck), lime putty and hydraulic lime (Fornace di calce Fagotti, Mercatale V.P., Florence, Italy) were added at different concentrations to the OMW.

The use of lime putty at a concentration range included from 10 to 40 g/L provided the worst results, giving rise to a COD and TSS removal of only a few percentage units. Moreover, the pH increased to values as high as 10, which are incompatible with the survival of the reeds.²⁷

The addition of calcium hydroxide at a concentration of 6 g/L provided a removal of COD and TSS of 12 and 40%, respectively. The pH was around 8, a value usually considered as the upper limit of the tolerance range for *Phragmites*.²⁷

Among the tested materials, the best results in terms of reduction of organic carbon and settleable solids were observed with 2 g/L of hydraulic lime, which allowed a TSS removal of 40% and a decrease in COD and BOD₅ of about 30%. With this kind of treatment, pH values in the range 6.12-6.51 were found.

Based on these results, 80 g portions of hydraulic lime were added in a hopper, under stirring, to 40 L aliquots of OMW and the resulting suspension was settled for 24 hours. The OMW pH reached values up to 7.9 immediately after the treatment with hydraulic lime and became steady at around 6.5 during the following 12 hours. With this method a total amount of about 500 L of OMW was pre-treated. The liquid phase was separated from the solid fraction and stored in tanks until its use for dosage experiments. An aliquot was taken from each tank and analysed (see Table 1). The mean removals were 28.8% and 26.3% for COD_T and COD_S, respectively, 30% for BOD₅ and 42.2% for TSS. The pH of the treated OMW was in the range 5.98-6.68 (mean 6.28) and, therefore, was consistent with the growth of reeds and microorganisms.

TABLE 1 - Mean values, standard deviation (n=12) and ranges determined for pH, COD_T (Total COD), COD_S (COD of filtered wastewater), BOD₅ and TSS in OMW before and after the treatment with 2 g/L of hydraulic lime, subsequent settling for 24 hours and separation of the aqueous upper phase.

Parameter	Before treatment	After treatment
pH	5.24±0.19 (5.02-5.41)	6.28±0.25 (5.98-6.68)
COD _T (g/L)	153.3±6.6 (147.4-162.3)	109.1± 19.4 (85.0-135.1)
COD _S (g/L)	129.1±7.1 (118.4-135.5)	95.1± 16.4 (74.5-118.0)
BOD ₅ (g/L)	29.0±3.6 (23.6-31.1)	20.2± 3.5 (16.0-25.0)
TSS (g/L)	32.5±3.3 (30.5-38.5)	18.8± 7.2 (10.6-29.4)

OMW treatment by the SSF-h constructed wetland at the dilution ratio 1/3 (v/v)

OMW, pre-treated as described above, was diluted 1/3 (v/v) with the effluent of an activated sludge plant (ASP) and dosed in the pilot wetland at a flow rate of 0.024 m³/d. TSS were efficiently removed, since a mean reduction of about 85% and an effluent concentration lower than 1 g/L was found. COD removal was about 50% both for filtered and unfiltered samples, while total polyphenols showed a decreasing trend of the removal as the time increased, with effluent concentrations similar to those determined in the inlet, just 12 days after the start of the research. In addition, a strong suffering of *Phragmites* was observed.

This behaviour suggested that the plant was overloaded and, therefore, the experiment was interrupted and the reed bed was fed with the ASP effluent, until outlet TSS, COD_T and polyphenols were the same observed before the OMW dosage.

OMW treatment by the SSF-h constructed wetland at the dilution ratio 1/10 (v/v)

OMW was diluted 1/10 (v/v) with the ASP effluent and, starting from 24 May 2001, dosed in the reed bed at a flow rate of 0.024 m³/d.

Effluent pH values were always higher than those measured in the influent (mean and standard deviation: 6.44±0.35) and were included between 7 and 8 (mean and standard deviation: 7.45±0.44), with the exception of the first two weeks of operation, which cannot be considered as a period of standard working conditions.

Inlet TSS concentrations ranged from 243 to 1219 mg/L (mean and standard deviation 641±248 mg/L) and were significantly lower than those measured after the pre-treatment with lime putty and subsequent settling. This was due to a further sedimentation process occurred during the storage of OMW, before their use for the dosage experiment. Outlet TSS concentration showed a higher variation (range: 135-2439 mg/L; mean and standard deviation 806±923 mg/L), partially depending on the different extent of evapotranspiration (corresponding to the different wetland temperatures) which involve a concentration effect of the effluent.

The amounts (g/d) of suspended solids determined in the influent and in the effluent of the pilot system are reported in Figure 3a. TSS were efficiently removed during the period May – July (mean removal percentage and standard deviation: 73.9±14.9), according to the general consensus that constructed wetlands are able to remove all settleable and floatable solids by sedimentation and filtration, and colloidal solids by adsorption to bacteria and plant tissues.²⁸ However, starting from August and up to the middle of September, very poor performances were observed, with outlet values often higher than inlet ones. This behaviour could be due both to saturation phenomena, and to the wetland temperature increase, that could have given rise to a less efficient sedimentation and to the desorption of particulate material previously trapped into the reed bed. The significant linear correlation ($R^2=0.36$, $P<0.01$) found when TSS removal percentages were plotted as a function of wetland temperatures (graph not shown) supported the last hypothesis.

Total-P and TKN showed rather similar concentrations in the inlet (ranges: 10-64 and 40-131 mg/L, respectively), while in the outlet a greater difference between the two parameters was observed (ranges: 3-61 and 36-560 mg/L, respectively). The trends of the daily amounts of Total-P and, above all, TKN were similar to that described for TSS. A very good removal percentage (mean and standard deviation: 79.3±16.1) was observed for phosphorus from the starting of the study up to the end of August. A significant reduction was also registered for TKN during the period May-July (mean removal percentage and standard deviation: 50.8±18.0). However, effluent amounts much higher than the inlet ones were found both for P and TKN for a few samples collected in the period August-September (see Figures 4a and 5a).

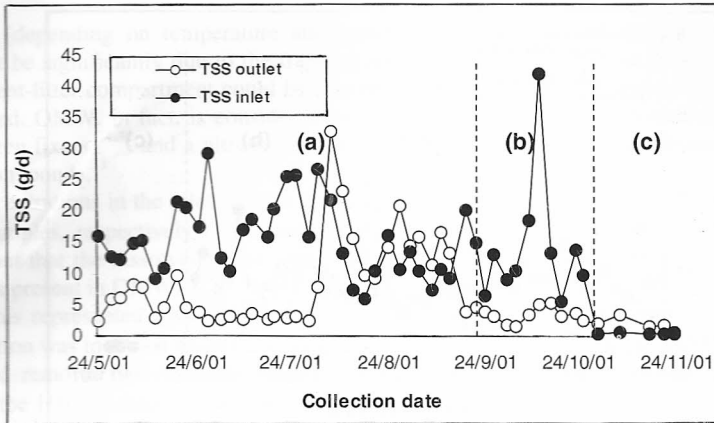


FIG. 3 - TSS amounts (g/d) in the influent and effluent during the whole period of operation. (a) dosage of wastewater diluted 1/10 v/v; (b) recycling of effluent wastewater; (c) post-dosage.

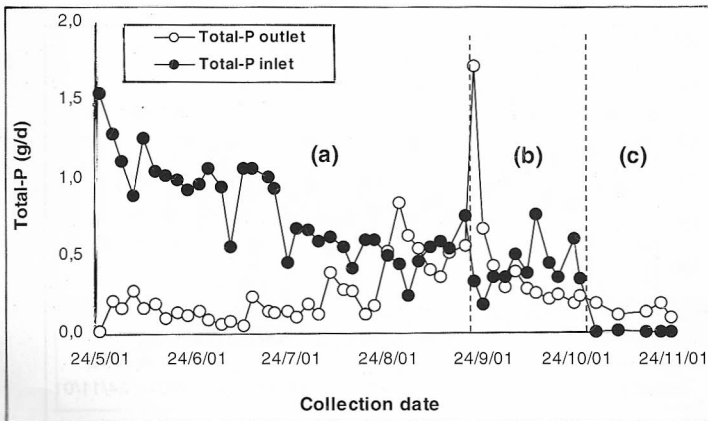


FIG. 4 - Total P amounts (g/d) in the influent and effluent during the whole period of operation. (a) dosage of wastewater diluted 1/10 v/v; (b) recycling of effluent wastewater; (c) post-dosage.

It should be noted that, in the same period, organic matter did not show outlet values higher than the inlet ones, as illustrated from COD_T data (see Figure 6a). This behaviour pointed out that solids settled into the bed are subjected to an enrichment in phosphorus and nitrogen with respect organics and suggested that removal mechanism for organic material involved mainly a real degradation, while nitrogen and phosphorus seemed to be removed by sorption. Removal of N and P in constructed wetlands can occur by plant uptake, microbiological processes and physico-chemical mechanisms.²⁸

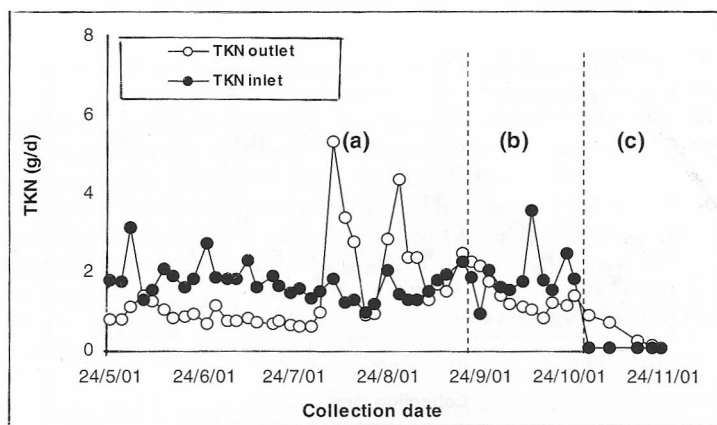


FIG. 5 - TKN amounts (g/d) in the influent and effluent during the whole period of operation. (a) dosage of wastewater diluted 1/10 v/v; (b) recycling of effluent wastewater; (c) post-dosage.

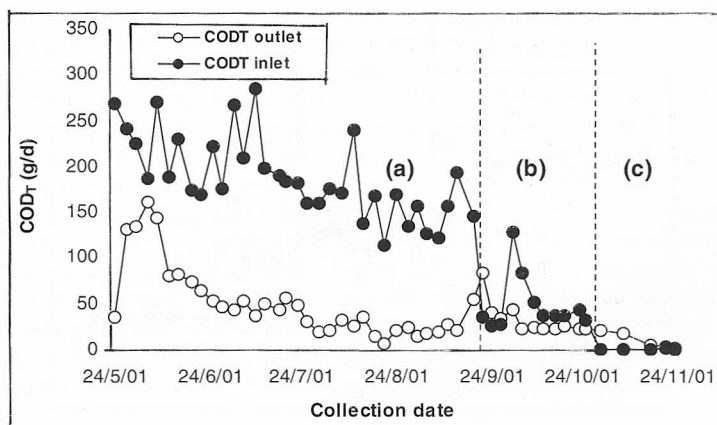


FIG. 6 - COD_T amounts (g/d) in the influent and effluent during the whole period of operation. (a) dosage of wastewater diluted 1/10 v/v; (b) recycling of effluent wastewater; (c) post-dosage.

The amount of nutrients that can be removed by plant uptake and subsequent harvesting usually constitutes only a small fraction of the quantity loaded into these systems with domestic wastewater and, particularly, with OMW.²⁹ Sorption of P on the wetland medium and/or on solid particles which can be trapped into the bed by sedimentation and/or filtration, is the main mechanism for its abatement in horizontal flow constructed wetlands.³⁰ The presence of significant amounts of phosphorus in the particulate matter released from the bed is therefore expected. On the other hand, organic nitrogen is usually implicated in ammonification and nitrification/denitrification biological

processes (depending on temperature and concentration of dissolved oxygen) and its removal should not be significantly due to the trapping into the bed.¹⁵ However, an increase of nitrogen in the sediment-litter compartment could be also due to its fixation by the biological material present into the bed. OMW, in fact, is considered by many authors a suitable substrate for the growth of free nitrogen fixers^{31,32} and a nitrogen increase has been observed in sludge from OMW stored in evaporation ponds.³³

COD concentrations in the inlet were in the ranges 4710-11880 and 4170-10530, for unfiltered and filtered samples, respectively (mean and standard deviation: 7835 ± 1864 and 6593 ± 1822 mg/L), pointing out that the dissolved phase accounted for the most part (about 85%) of the total organic substances present in OMW.

Polyphenols represented a noteworthy part of the organic fraction of OMW: in fact, their inlet concentration was in the range 661-2510 mg/L (mean and standard deviation: 1457 ± 467 mg/L).

Very good removal performances were observed for COD_T during the whole period of OMW dosage at the 1/10 v/v dilution ratio (mean removal percentage and standard deviation: 74.1 ± 17.6).

An almost identical trend was observed for COD_S (graph not shown) and for polyphenols (see Figure 7a), which removal was, surprisingly, constantly high (mean removal percentage and standard deviation: 83.4 ± 17.8).

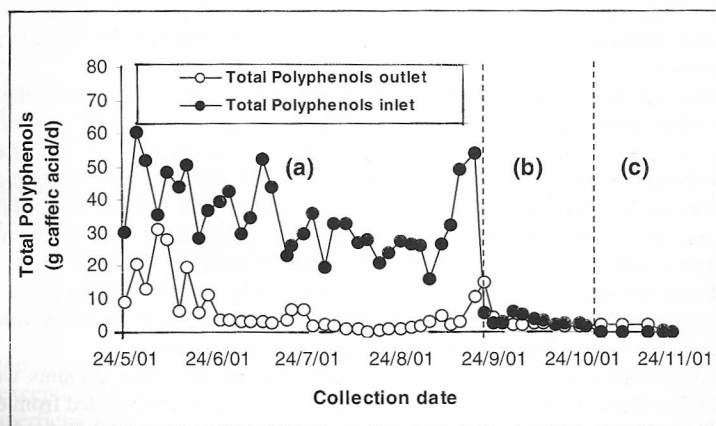


FIG. 7 - Total polyphenols (expressed as g caffeic acid/d) in the influent and effluent during the whole period of operation. (a) dosage of wastewater diluted 1/10 v/v; (b) recycling of effluent wastewater; (c) post-dosage.

Removals of COD_S and polyphenols were linearly related to the wetland temperature ($R^2=0.61$ $P<0.01$ and $R^2=0.60$ $P<0.01$, respectively) confirming that degradation phenomena contributed to the reduction of these parameters. These findings are in agreement with the results obtained by Sacco et al. (2004) in a study concerning the removal of alkylphenol polyethoxylates in a horizontal flow reed bed.³⁴

In spite of the high removal percentage, it should be underlined that outlet COD and polyphenol concentrations remained high and were included in very wide ranges (COD_T : 1120-7510 mg/L; COD_S : 908-7500 mg/L; polyphenols: 28-1450 mg/L). As above-mentioned for TSS, this strong

variability can be partly ascribed to a concentration effect of the effluent due to evapotranspiration phenomena. Moreover, in the first two weeks of operation (which cannot be considered as a period of standard working conditions) outlet concentration significantly higher than those determined in the following period, were observed.

Recycling of effluent wastewater

Recycling of the effluent was very effective for the removal of TSS, being the mean removal percentage equal to 70.4 ± 16.2 . Nevertheless, concentration of suspended material in the outlet remained in the range 73-244 mg/L.

As regard the other parameters, outlet concentrations significantly higher than those determined in the inlet were found for the first two or three samplings after the beginning of the recycling experiment (see Figures 3b-7b). However, positive removal percentages for all the examined parameters were observed afterwards: the lowest abatement was found for COD_s (26.5 ± 17.8) and the highest for COD_T (47.2 ± 16.1); intermediate performances were obtained for TKN, total phosphorus and polyphenols (34.5 ± 24.0 , 38.9 ± 19.8 and 34.2 ± 18.6 , respectively).

Post dosage and mass balance of the pollutants

After the end of the recycling, the reed bed was fed for about one month with the effluent of the ASP, previously used for the dilution of OMW in the experiments of dosages at the dilution ratios 1/3 and 1/0 v/v. This investigation allowed us to know if sorption processes were reversible and to obtain important information about the relevance of this mechanism in the abatement of the different parameters.

Effluent pH was included in the range 7.47-8.03 and was slightly higher than the influent one (range: 7.19-7.84), pointing out that the bed does not have a residual acidity due to the accumulation of acid compounds such as polyphenols. According to this finding, outlet concentration of polyphenols was less than 100 mg/L since from the first sampling. A strongly decreasing trend was observed afterwards and effluent concentration dropped up to about 2 mg/L. A similar trend was registered also for the other parameters, which outlet concentrations reached the following values: COD_T 98 mg/L, COD_s 95 mg/L, TSS 22 mg/L, Total-P 4.1 mg/L and TKN 3.0 mg/L. Such values are much lower than those obtained during the post-dosage study and, with the exception of polyphenols, were perfectly compatible with Italian regulations concerning wastewater discharge in surface water.³⁵ Therefore, the experiment was interrupted.

In order to estimate the mass balance for the different parameters, their amounts were evaluated from the dispersion plots reported in Figures 3-7, calculating the area subtended from each plot by a succession of trapeziums. According to this calculation method, the area delimited by two outlet consecutive experimental points (a rectangular trapezium) is subtracted from the corresponding trapezium of the inlet, obtaining the amount removed by the pilot scale wetland in the examined period.

As shown by Table 2, the overall removal for the investigated parameters, with the exception of TKN, was good and suggested that constructed wetlands are able to treat OMW efficaciously. In addition, the amount of pollutants released during the post-dosage experiment was low, being included from 3.4% (TSS) and 6.9% (Total-P) of the total amounts flowed out of the system during the whole period of study.

TABLE 2 – Mass balance (g) of the different parameters during the whole study period.

Parameter	Inlet	Outlet	Removed amount	Removal (%)
COD _T	24368	7570	16798	68.9
COD _S	19970	6761	13209	66.1
TSS	2415	1223	1192	49.4
Total-P	110	50	60	54.5
TKN	282	247	35	12.4
Polyphenols	4369	929	3440	78.7

CONCLUSIONS

The present investigation has produced useful information for the application of full-scale experiments to OMW treatment, using both multi-stage horizontal plants and systems with recycling of effluent wastewater. OMW, in fact, being produced in a short period, can be dosed in a reed bed at very little hydraulic loading rates and/or after dilution, taking advantage of the elapsing time between two subsequent oil campaigns.

Pre-treatment of OMW (in order to reduce the concentration of suspended solids) and subsequent dilution (to decrease the concentration of polyphenolic antimicrobial substances) are essential for the application of OMW in constructed wetlands.

Although the experiment of OMW dosage 1/10 (v/v) was carried out in under-dimensioning conditions (average TSS, COD and polyphenol loads: 180, 220 and 40 g/m²d, respectively), good removal performances were achieved for suspended solids and organic matter.

Results from recycling experiment seemed as good as to make it useful for a significant improvement of the wastewater quality when a number of recycling cycles were performed. Therefore, an accurate cost-analysis should be made in order to assess the economic sustainability of this process.

Effluent concentrations for the different parameters after one month of post-dosage were low and, with the only exception of polyphenols, compatible with Italian regulations concerning wastewater discharge in superficial waters. This demonstrated that the amount of pollutants trapped into the bed at the end of recycling was low and suggested that the plant could be used for the treatment of OMW from subsequent oil campaigns.

The chemical characteristics of the effluent make it suitable for agricultural reuse without phytotoxic effects on soil and should encourage the full-scale application of reed beds in rural areas. In addition, a low hygienic-health impact is expected, taking into account of the antibacterial characteristics of OMW and of the good performances of SSF-h systems in pathogen removal.³⁶ However, further studies on full scale systems need in order to confirm the results obtained in this research, particularly concerning the maintenance of the observed performances during consecutive operation years. In this regard the use of natural medium amended with materials having high P-binding capacity, such as calcite, could be very useful.³⁷

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